

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 770 634 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
02.05.1997 Bulletin 1997/18

(51) Int. Cl.⁶: **C08G 18/50**, C08F 20/28,
C08F 20/36, C08G 63/682,
C08G 65/00

(21) Application number: 96202894.0

(22) Date of filing: 21.10.1996

(84) Designated Contracting States:
CH DE FR GB IT LI NL

(30) Priority: 23.10.1995 NL 1001472
23.10.1995 NL 1001471

(71) Applicant: Océ-Nederland B.V.
5914 CC Venlo (NL)

(72) Inventors:
• Tazelaar, Frans Willem
5912 HR Venlo (NL)

• Markies, Peter Richard
5971 DP Grubbenvorst (NL)
• Van den Reek, Johannes Adrianus
5644 KA Eindhoven (NL)
• Van der Stappen, Cornelis Johannes Maria
6524 HE Nijmegen (NL)

(74) Representative: Hanneman, Henri W.A.M. et al
Océ-Nederland B.V.
Patents and Information
St. Urbanusweg 43
P.O. Box 101
5900 MA Venlo (NL)

(54) **Lengthened difunctional perfluoropolyether oils and rubbers prepared therewith**

(57) The invention relates to a difunctional perfluoro-polyether oil, prepared by reacting a perfluoropolyether diol oil having a weight averaged molecular weight (Mw) between 1500 and 3000 with a chain lengthener from the group of diacid chlorides and diisocyanates, and to perfluoropolyether rubbers prepared by means of these chain-lengthened oils.

EP 0 770 634 A2

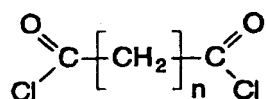
Description

The invention relates to difunctional perfluoro-polyether oils and rubbers prepared by means of such oils. Oils of this kind are known from D Sianesi, Organofluorine Chemistry 1995, page 435. The properties of perfluoropolyether oils are very favourable for use as oils, lubricants in car waxes, and so on. The functional oils are suitable as an intermediate product in the preparation of rubbers, release coatings and the like. One disadvantage, however, is that these oils have a relatively low molecular weight and this restricts their range of application.

The object of the invention is to provide difunctional perfluoropolyether diols via a simple synthesis route with much higher molecular weights. To this end, lower molecular difunctional perfluoropolyether diols are lengthened with a chain lengthener chosen from the group of diisocyanates and diacid chlorides.

In one embodiment of the invention, the diisocyanate chain lengthener used is a difunctional diisocyanate perfluoropolyether oil. The resulting difunctional perfluoropolyether oils may have OH or NCO terminal groups depending on the diol: diisocyanate ratio. Starting with molecular weights of 2000 - 2500 for the starting diol and the starting diisocyanate, it is a simple matter to obtain molecular weights of chain-lengthened perfluoropolyether oils of about 6000 to about 25000.

In another embodiment of the invention, the diacid chloride used is



where $n = 0 - 4$ and the chain lengthener used is preferably glutaryl dichloride. Starting with a molecular weight of between 2000 and 2500 of the starting diol, it is possible to obtain molecular weights of between 4000 and 25000 for chain-lengthened perfluoropolyether oils.

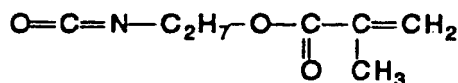
After cross-linking to form a rubber, these lengthened difunctional perfluoropolyether oils are very suitable as top layer rubber, e.g. in fixing devices in hot roll fusers, as top layer rubber on an intermediate medium as described in EP 0 581 355, as adhesive coatings, release coatings, and so on. After curing they are also suitable as anti-wetting coatings for nozzle plates of inkjet printheads.

This cross-linking can be carried out in various ways. One of the ways is so to derivatise the functional terminal groups of the chains that curing becomes possible under the influence of light, heat and/or moisture.

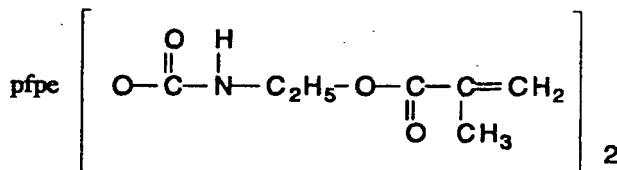
In a first embodiment of the method for the rubber cross-linking, the OH-groups of a chain-lengthened perfluoropolyether diol are esterified with an acryloyl chloride.

Cross-linking then takes place with UV light in the presence of a photo-initiator at higher temperatures. Cross-linking can also be effected by heating in the presence of a peroxide.

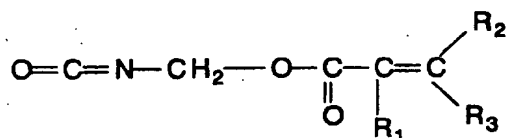
In a second embodiment of the method for rubber cross-linking, the OH groups in a chain-lengthened perfluoropolyether diol HO-pfpe-OH are converted with a urethane acrylate compound, such as



to perfluoropolyether



For this, isocyanate acrylates according to the molecular formula



where $p = 1 - 5$ and R_1 , R_2 and R_3 can be jointly and independently chosen from H and a lower alkyl group, chosen from the group methyl, ethyl, n-propyl, isopropyl, n-butyl, and t-butyl.

Cross-linking then takes place in the same way as in the first embodiment.

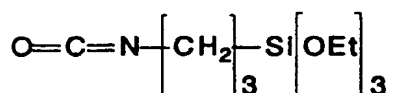
Suitable catalysts for the curing of urethane perfluoropolyethers are dibutyl tin dilaurate, dibutyl tin oxide, various iron derivatives such as ferroacetyl acetate, tertiary amines etc, in quantities from 0.001 to 2 % by weight. Perfluoropolyethers with (meth)acrylate or urethane (meth)acrylate terminal groups can be cross-linked

1) with the aid of peroxides such as dibenzoyl peroxide, 2,5-bis(ter-butylperoxy)-2,5-dimethylhexane, ter-butylperoxybenzate, benzophenone, etc in quantities from 0.1 to 3 % by weight in combination with heat ($> 100^\circ\text{C}$) and

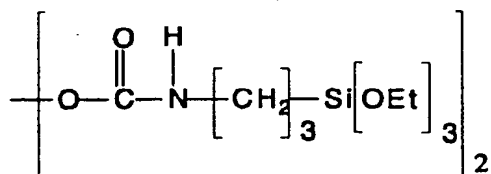
2) with the aid of photo-initiators such as α, α -diethoxyacetophenone, o-nitrobenzene diazonium hexafluoroantimonate, fluorenone, triphenyl amines, benzoin alkyl ethers, carbazole, etc, in combination with UV light.

Acrylate reactive perfluoropolyethers according to the invention are very suitable as an additive to improve surface properties (non-wetting, antistatic) in UV or EB (electron beam) curing coatings based on various acrylates or methacrylates. There are applications in the area of paper coatings, coating of plastics and glass articles and the like.

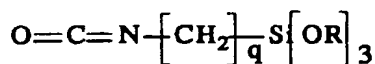
In a third embodiment, the OH groups of a chain-lengthened perfluoropolyether diol are converted with



to perfluoropolyether



In general compounds from the group



where $q = 1-4$ and R chosen from the group methyl, ethyl, n-propyl and i-propyl, can be used.

Cross-linking then takes place under the influence of a catalyst such as tin octoate with water and with temperature elevation. It is a simple matter to cure these rubbers in air. One of the particular advantages of these transparent rubbers is the good conductivity. A thin layer of perfluoropolyether rubber according to the invention charges up barely if at all, even after long periods of charging (up to 1 kV).

It has surprisingly been found that the prepared perfluoropolyethers as described above with $-\text{NH}-\text{C}(\text{O})$ -sequences in the terminal group, such as triethoxysilyl and urethane acrylate, preferably chain-lengthened with a coupler giving rise to $\text{C}=\text{O}$ - or other polar groups in the main chain, exhibit a surface resistance of the order of magnitude of $10^8 - 10^9 \Omega\text{cm}$. This is a factor 100 - 1000 lower than the surface resistance of perfluoro-polyethers based on urethane cross-linking ($10^{12} \Omega\text{cm}$) and various other unfilled elastomers, such as (fluoro)- silicone rubber. This property makes the lay-

ers based on the said perfluoropolyethers intrinsically antistatic.

Although we do not wish to speculate about the conducting mechanism in the perfluoropolyethers layers, a possible explanation can be sought in the presence of ions in the product, caused by the various steps in the preparation, by which a form of ion-conductivity can arise in the layer.

5 Control of this ion-conductivity in perfluoropolyether products (oils and rubbers) can be done via two mechanisms: via variation of the molecular structure, so via the introduction of polar relaxation mechanisms using polar groups, for example by the introduction of polyethylene oxide groups in the polymer chains and via the addition and variation of various ions, such as quaternary ammonium salts and lithium salts to the perfluoropolyether matrix.

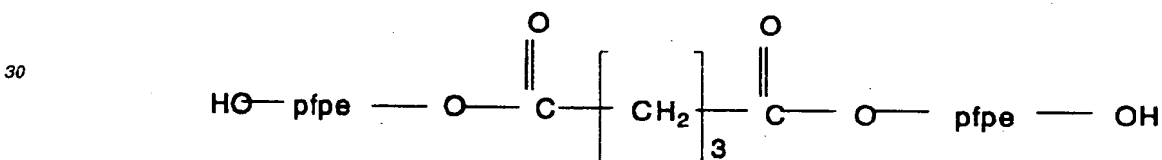
10 Possible applications are in the area of using these layers as transparent top layers on intermediates as described in EP 0 581 355, transparent conductive toner coatings, transparent non-stick coatings on photoconductors and other image-forming media, as indicated, for example, in US 5 319 334, on transport rollers and the like. Other possible applications where transparency and conductivity are necessary are, for example, in the motor vehicle industry, the carpet industry, and optical instruments.

15 In order further to improve the mechanical properties, it is possible to cross-link mixtures of chain-lengthened perfluoropolyether oils provided with reactive groups. The elastic properties and tearing strength can be controlled by correct choice of the reactants.

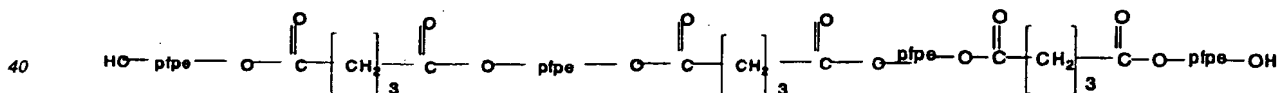
The invention will now be described in greater detail with reference to a number of examples.

Example 1

20 Chain lengthening of lower molecular OH terminated perfluoropolyether oils was performed as follows in a 3-neck flask provided with a top agitator, dropping funnel (with gas circulation) and a spherical condenser. The flask was continuously washed with nitrogen. 500 g of OH terminated perfluoropolyether oil, HO-perfluoropolyether-OH, with a mass averaged molecular weight, MW = approximately 2150 g/mol were weighed into the 3-neck flask. 10.2 g of glutaryl dichloride was added dropwise in 1 hour via the dropping funnel with agitation at 0°C. After 24 hours at 100°C a viscous substantially clear light orange liquid was obtained. This oil



35 can be converted to rubber in the same way as in Example 2. The above reaction can also be repeated by reacting the product of the reaction with glutaryl dichloride again under the same conditions. The result



is the formation of:

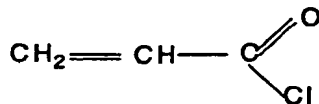
45 This compound theoretically has an MW of about 8900 g/mol. In practice, MWs of 6500 (100°C, 24 hours) and 11000 (160°C, 24 hours), can be found depending on the reaction temperature. This oil can also be further extended in the same way by again reacting the product for 24 hours at 100°C with glutaryl dichloride. In this way an OH terminated perfluoropolyether oil was synthesised with an MW of 11000 and with an MW of 25000 g/mol in the case of reaction at 160°C.

50 All these oils can be converted to a rubber in the same way as in Example 2.

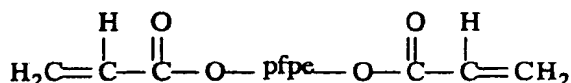
Example 2

98.1 g (11.2 mmol) of perfluoropolyether diol (HO-perfluoropolyether-OH) 25 g of 1,1,2 trifluorotrichloroethane and 5 g of triethylamine were cooled in an ice bath to 0°C in a 250 ml 4-neck flask provided with an agitator, nitrogen inlet, a closed dropping funnel (with gas circulation) and a spherical condenser. 3 g (33.1 mmol) of acryloyl chloride

55



was dissolved in 40 g of 1,1,2 trichlorotrifluoro-ethane in the dropping funnel. This solution was added dropwise with agitation to the mixture in the 4-neck flask. The resulting white-yellow dispersion was kept at 55°C for 1 hour, whereupon 50 ml of ethanol was added. The resulting strongly yellow mixture was then agitated for 15 minutes at 50°C whereupon it was cooled. The acrylate-terminated oil obtained in this way was washed with a 1,1,2 trichlorotrifluoro-ethane/ethanol mixture. After evaporation of the solvents, 87 g (yield 88%) of a clear light-brown acrylate terminated oil remained:

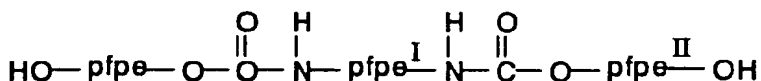


This oil was mixed with a photo-initiator, 20 µl of 2,2 diethoxyacetophenone per 10 g of acrylate terminated oil.

This mixture was applied as a top layer to a metal cylinder provided with an approximately 20 mm thick layer of peroxide hardened silicone rubber. The approximately 60 µm thick top layer was then cured in a nitrogen atmosphere by means of a UV lamp. The resulting clear rubber is strong and elastic. The glass transition temperature of the rubber is about -125°C.

Example 3

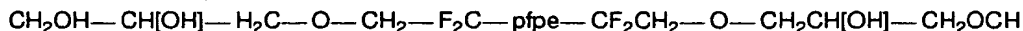
Chain lengthening on the basis of a urethane reaction was carried out in a 250 ml reaction vessel with a top agitator, nitrogen inlet and a thermometer. 50.6 g of OCN-perfluoropolyether-NCO with an Mw of 2562 g/mol, 89.3 g of HO-perfluoropolyether-OH with an Mw of 2258 g/mol and 1.5 g of 1 Mn catalyst solution 1 W% solution (dibutyl tin dilaurate in 1,1,2 trichloro-trifluoroethane) were reacted together. This reaction mixture was heated for 1 hour at 75°C under nitrogen. The resulting lengthened perfluoropolyether oil



was then provided with acrylate end groups via the method of Example 1. By means of benzoyl peroxide and heat, the oil provided with 2.5% carbon black was finally converted to a top layer rubber. The mixture with benzoyl peroxide was for this purpose placed in a layer about 60 µm thick on a substrate. The layer was then cured at a temperature of about 140°C.

Example 4

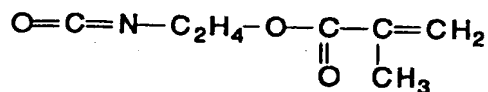
A rubber was made in the same way as in Example 3, an 80:20 mixture of a perfluoropolyether HO - pfpe - OH, and a perfluoropolyether tetraol being used as perfluoropolyether diol.



The presence of the tetraol perfluoropolyether increased the cross-link density after cross-linking with, for example, acrylate groups in the resulting rubber, so that the rubber hardness was increased.

Example 5

184.1 g of perfluoropolyether diol with an Mw of about 2200, 19.55 g of 2-isocyanatoethyl methacrylate



and 0.11 g of dibutyl dilaurate were stirred for 4½ hours at room temperature in a 3-neck flask with a condenser, agitator and nitrogen inlet. The resulting product was worked up with 1,1,2 trifluorotrichloro-ethane and stirred with 20 µl of diethoxyacetophenone per 10 g of perfluoropolyether oil. The product was then cured in one operation in a nitrogen atmosphere by means of a UV lamp (UV-C: wavelength about 360 nm).

After about 15 minutes a well-cured clear antistatic rubber was obtained.

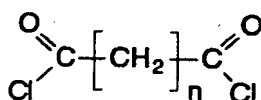
Example 6

61.85 g of chain-lengthened perfluoropolyether diol according to Example 2 with an Mw of about 11000, 2.95 g of 3-(triethoxysilyl) propylisocyanate and 0.65 g of catalyst solution (1 w% dibutyl tin dilaurate in tetrahydrofuran) was agitated at room temperature for 15 hours. NMR analysis of the resulting clear oil showed that the OH groups of the chain-lengthened perfluoropolyether diol were completely converted.

The oil was then mixed with 1 w% tin octate. The resulting mixture was applied in a layer approximately 60 µm thick to a fabric belt provided with about 2.5 mm peroxide hardened silicone rubber. This perfluoropoly-ether layer was air cured for about 4 hours. The resulting non-stick clear rubber had good visco-elastic properties.

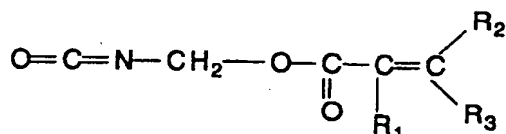
Claims

1. Difunctional perfluoropolyether oil, characterised in that the oil is prepared by reacting a perfluoropolyether diol oil having a weight averaged molecular weight (mw) between 1500 and 3000 with a chain lengthener from the group of diacid chlorides and diisocyanates.
2. Difunctional perfluoropolyether oil according to claim 1, characterised in that the diisocyanate used is a difunctional diisocyanate perfluoropolyether oil.
3. Difunctional perfluoropolyether oil according to claim 1, characterised in that the chain lengthener used is a diacid chloride having the molecular formula

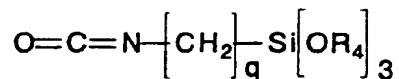


where n = 0 - 4.

4. Difunctional perfluoropolyether oil according to claim 3, characterised in that the diacid chloride used is glutaryl dichloride.
5. Perfluoropolyether rubber, characterised in that the rubber is prepared from derivatised perfluoropolyether diol oil chain-lengthened according to any of claims 1 to 4, wherein the OH terminal groups are derivatised with a compound from the group of acryloyl chlorides, isocyanate acrylates according to the molecular formula



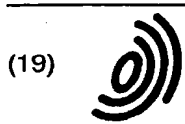
where $p = 1 - 5$ and R_1 , R_2 and R_3 can be jointly and independently chosen from H and a lower alkyl group, chosen from the group methyl, ethyl, n-propyl, isopropyl, n-butyl, and t-butyl or with a compound from the group



where $q = 1 - 4$ and R_4 can be chosen from the group methyl, ethyl, n-propyl and i-propyl, whereafter these derivatised perfluoropolyether oils are cross-linked under the influence of a suitable catalyst.

6. Perfluoropolyether rubber according claim 4 characterized in that said rubber is prepared using as derivatized perfluoropolyether diol oil having a surface resistance of approximately 10^8 - $10^9 \Omega \text{cm}$.

THIS PAGE BLANK (USPTO)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 770 634 A3**

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
14.05.1997 Bulletin 1997/20

(51) Int. Cl.⁶: **C08G 18/50**, C08F 20/28,
C08F 20/36, C08G 63/682,
C08G 65/00

(43) Date of publication A2:
02.05.1997 Bulletin 1997/18

(21) Application number: 96202894.0

(22) Date of filing: 21.10.1996

(84) Designated Contracting States:
CH DE FR GB IT LI NL

(30) Priority: 23.10.1995 NL 1001472
23.10.1995 NL 1001471

(71) Applicant: Océ-Nederland B.V.
5914 CC Venlo (NL)

(72) Inventors:
• Tazelaar, Frans Willem
5912 HR Venlo (NL)

- Markies, Peter Richard
5971 DP Grubbenvorst (NL)
- Van den Reek, Johannes Adrianus
5644 KA Eindhoven (NL)
- Van der Stappen, Cornelis Johannes Maria
6524 HE Nijmegen (NL)

(74) Representative: Hanneman, Henri W.A.M. et al
Océ-Nederland B.V.
Patents and Information
St. Urbanusweg 43
P.O. Box 101
5900 MA Venlo (NL)

(54) **Lengthened difunctional perfluoropolyether oils and rubbers prepared therewith**

(57) The invention relates to a difunctional perfluoro-polyether oil, prepared by reacting a perfluoropolyether diol oil having a weight averaged molecular weight (Mw) between 1500 and 3000 with a chain lengthener from the group of diacid chlorides and diisocyanates, and to perfluoropolyether rubbers prepared by means of these chain-lengthened oils.

EP 0 770 634 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 20 2894

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 4 933 408 A (GOLDENBERG MERRILL) 12 June 1990 * claim 1 * * column 4, line 41 - line 68 * * column 5, line 34 - line 54 * * column 7, line 49 - line 62 * ---	1,2	C08G18/50 C08F20/28 C08F20/36 C08G63/682 C08G65/00
X	EP 0 621 298 A (AUSIMONT SPA) 26 October 1994 * claims 1,4-9 * * page 3, line 6 - line 33 * * example 1 * ---	1,2	
A	EP 0 322 624 A (SIEMENS AG) 5 July 1989 * claims 1-3 * * page 2, line 12 - line 39 * ---	1	
A	EP 0 622 391 A (AUSIMONT SPA) 2 November 1994 * claims 1-3,6 * * page 3, line 8 - page 4, line 6 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C08G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19 February 1997	Examiner Van Puymbroeck, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure F : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 QLEZ (P04C01)